Journal of Innovative Materials in Extreme Conditions
2021
Volume 2
Issue 2

XRD ANALYSIS OF BORON DOPED GLASSY CARBON

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Abstract: *Glassy carbon samples containing boron are produced via two different procedures. Boron was introduced into the glassy carbon precursor to avoid the commonly used high temperature doping process and also to obtain the samples of glassy carbon with boron uniformly distributed throughout the bulk of a material. Structural analysis of specimens treated under different temperature-pressure conditions shows that boron enhances the structural ordering of all samples but not to the same extent, clearly indicating that boron in different samples occupies different structural positions.*

Keywords**:** *X-ray diffraction; glassy carbon; boron; graphitization*

1. Introduction

Glass-like carbons are usually obtained by pyrolysis of thermosetting resins around 1273 K. Due to their unique combination of properties including isotropy, chemical inertness, gas impermeability, high hardness, and wear resistance, glass-like carbons are used in a wide variety of applications, such as medical implants, high performance materials for the aerospace industry, electrochemical electrodes, fuel cell components and as essential material for silicon wafer processing equipment used in the manufacture of semiconductor devices [1,2]. Boron has a unique property as a substitutional element in the carbon structure. It can replace a carbon atom in the graphene layer thus altering numerous properties of the original carbon material: structure, thermal and electrical conductivity, oxidation stability, etc. [3-7]. One of the major disadvantages of employing doping as a route for the introduction of boron into carbon material is the necessity for high temperatures application during the doping reaction (usually around 3000 K) [8]. The other disadvantage of this widely employed boron doping strategy is the existence of a concentration gradient, *i.e.* the boron content in carbon material decreases with the depth of material.

The aim of this work was to examine the possibilities for the boron atoms introduction into the glassy carbon precursor to avoid high temperature doping process and also to obtain the samples of glassy carbon with boron uniformly distributed through the bulk of a material.

2. Experimental Procedures

Materials used in this investigation were as follows: resol type phenol-formaldehyde resin (»Latex«, Yugoslavia), boric acid (H_3BO_3) p.a., amorphous boron metal powder, p.a., ethyl alcohol (C_2H_5OH), p.a.

Boron was added into the matrix precursor (resin) in two different forms:
(i) – as boron oxide (B_2O_3), obtained during the H_3BO_3 thermal degradation, in an amount sufficient to obtain 4 wt.% of boron in a resulting glassy carbon (designated as *GCB1* in the further text) was dissolved in C_2H_5OH and this solution was then mixed with the resin which was also previously dissolved in C_2H_5OH.
(ii) – in the form of amorphous boron metal powder in an amount sufficient to obtain 4 wt.% of boron in a resulting glassy carbon (designated as *GCB2* in the further text).

Undoped glassy carbon is marked as *GC*.

All samples were heat treated at 350 K and 420 K to achieve the complete polymerization of the resin. Samples were then carbonized under an inert atmosphere of flowing nitrogen up to 1270 K with a heating rate of 12 K/h. In the next step carbonized samples were exposed to two different

treatments: at 2073 K in an atmosphere of flowing argon (*HTT*), and at 2073 K in an atmosphere of flowing argon with the simultaneous application of uniaxial pressure of 25 MPa (*HTT+P*).

Structural analysis of powdered samples was carried out by a Siemens D-500 powder diffractometer. The CuKα radiation was used in conjunction with a CuKβ nickel filter.

3. Results and Discussion

The X-ray diffraction patterns of the samples carbonized at 1273 K are given in Fig. 1. All investigated samples have two broad maxima corresponding to the (002) and (10) reflections of a turbostratic carbon structure typical for the *GC* structure [1]. The (002) reflection for the *GC* sample is very broad (full width at half maximum value, *FWHM*, is approximately 7°) and becomes even wider in the case of *GCB1* and *GCB2* samples (approximately 7.7° and 7.5°, respectively). Observed changes in 2θ, *i.e.* d_{002}, values are less than corresponding standard deviations, and the decrease of the d_{002} spacing in boron-containing samples cannot be unambiguously confirmed as it was reported in Ref [1]. Nevertheless, some important observations can be made. Namely, for the *GCB2* sample, a sharp reflection corresponding to the crystalline B_2O_3 (and/or H_3BO_3) was detected at 2θ = 28° which does not appear in the *GCB1* sample, nor the GCB sample in the Ref [1]. A small peak detected at 14.5° also belongs to B_2O_3. Obviously, B_2O_3 was formed in the *GCB2* sample during the sample preparation, probably as a result of the reaction of boron with released co-products of polymerization and carbonization, such as H_2O. Insert in the upper right corner of Fig. 1 shows the magnified encircled area of the *GCB2* sample with the arrow pointing to the diffraction peak present at 17.5° that belongs to the strongest reflection of the added elemental boron. The presence of this peak indicates that boron in the *GCB2* sample is partly present as B_2O_3 and partly as elemental boron. The absence of B_2O_3 or elemental boron reflections in the *GCB1* sample demonstrates that there is a difference in the nature between boron present in this sample and boron in the *GCB2* sample. It seems that boron, detected in the *GCB1* sample, was not formed as a separate phase and it was efficiently protected from reaction with the above-mentioned co-products. It should be mentioned that no reflections which may originate from H_3BO_3 or B_2O_3 could be observed in the X-ray diffraction patterns of the polymerized *GCB1* sample. This suggests that boron is uniformly distributed throughout the bulk of the material and presumably chemically bonded to the polymer cross-linked structure. Structural parameters obtained from the X-ray diffraction patterns of samples carbonized at 1273 K are presented in Table 1.

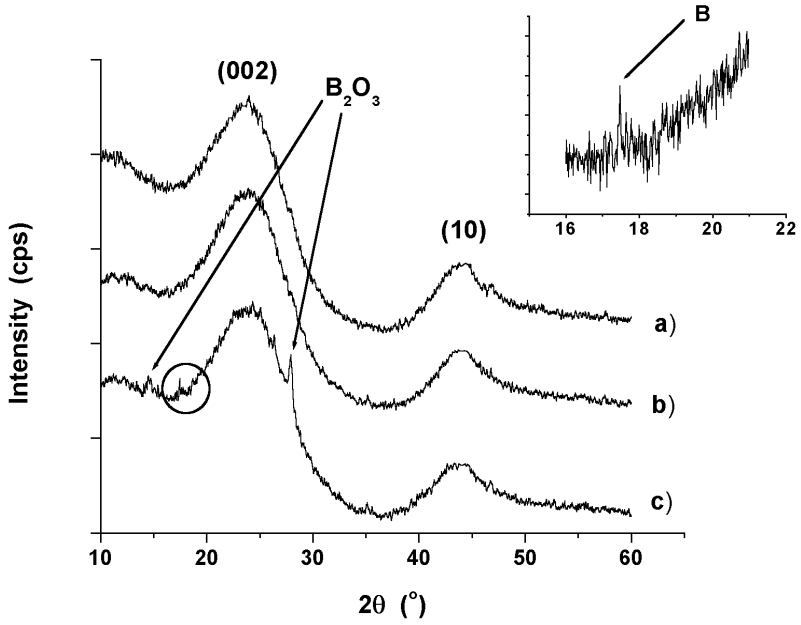

Figure 1. X-ray diffraction patterns of the samples carbonized at 1273 K: (a) GC; (b) GCB1; (c) GCB2.

Table 1. Structural parameters obtained from the X-ray diffraction patterns presented in Fig 1.

Sample	2θ (°)	d_{002} (nm)	FWHM (°)	L_c (nm)	n
GC	≈ 23.7	≈ 0.375	7.0	1.2	4
GCB1	≈ 23.4	≈ 0.380	7.7	1.1	4
GCB2	≈ 23.9	≈ 0.370	7.5	1.1	4

The X-ray diffraction patterns for the samples treated at 2073 K under ambient pressure are presented in Fig 2. Samples containing boron clearly show enhanced structural ordering and crystal formation indicated by the appearance of higher and narrower (002) reflections. The width of the (002) reflection (*FWHM*) is proportional to the crystallite size, *i.e.* crystallite thickness (L_c) and a number of graphene layers (*n*) present in the corresponding crystallite. Data presented in Tables 1 and 2 indicate that the temperature treatment at 2073 K significantly increases L_c and *n* values for all samples when compared with the values for the same samples treated at 1273 K.

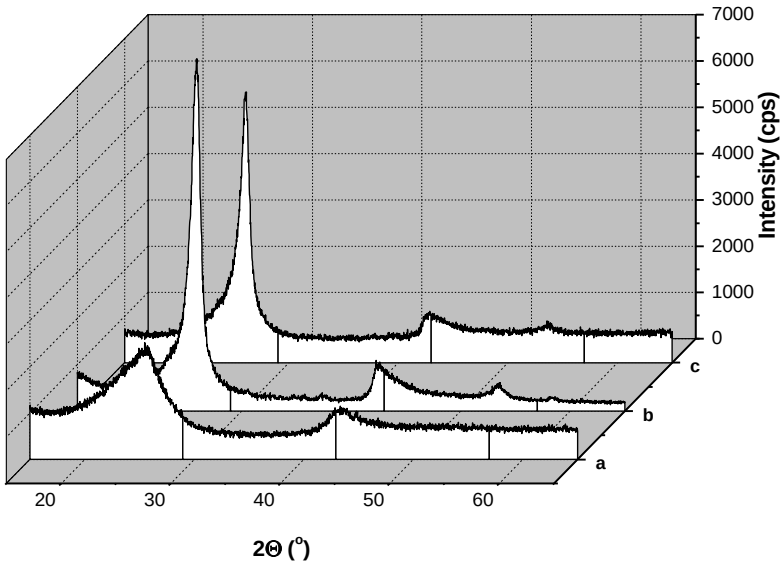

Figure 2. X-ray diffraction patterns of the samples treated at 2073 K: (a) GC; (b) GCB1; (c) GCB2.

Table 2. Structural parameters obtained from the X-ray diffraction patterns presented in Fig 2.

Sample	2θ (°)	d_{002} (nm)	FWHM (°)	L_c (nm)	n
GC	25.560	0.3482	4.3	1.9	6
GCB1	25.920	0.3435	1.0	8.2	25
GCB2	26.120	0.3409	1.0	8.2	25

The X-ray diffraction patterns for the samples treated at 2073 K under high pressure (25 MPa) are presented in Fig 3. The *GCB1* and *GCB2* samples are obtained as solid pellets while the GC sample remained powdered although an increase of the grain size was observed. It is obvious that the application of high pressure influenced the more efficient structural ordering of the *GCB1* sample than the *GC* and *GCB2* samples. This is clearly illustrated in Fig 3 by height and width of the (002) reflection and also by the data presented in Table 3, *i.e.* the *GCB1* sample exhibits the lowest d_{002} value and the highest L_c and *n* values. It may also be seen that only the *GCB1* sample possesses the clearly developed (004) reflection positioned at 2θ ≈ 54.2°, while the (10) reflection (2θ ≈ 43°) of glassy carbon is completely diminished. It is also important to observe that only in the X-ray diffraction pattern of the *GCB1* sample the reflections that presumably originated from the presence of B_4C appear. The appearance of these reflections implies that: 1) when the amount of boron in the carbon sample exceeds the substitutional solid solubility limit for a given temperature (≈ 1 wt.% at

2073 K) [10], B_4C reflections appear indicating that excess of boron is present in the interlaminar positions [9] between graphene layers, and 2) it is possible that solution-precipitation mechanism [9] involving B_4C plays an important role in enhancing structural ordering of the glassy carbon by forming the graphite domains in the disordered glassy carbon structure.

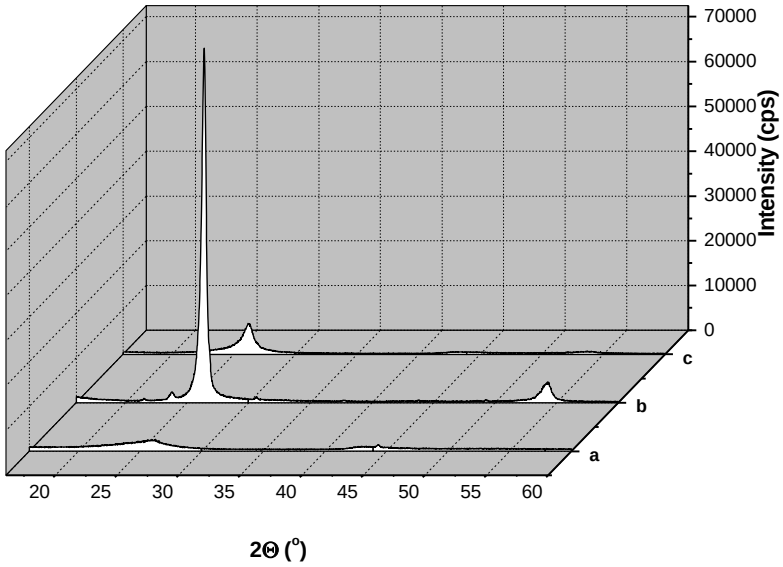

Figure 3. X-ray diffraction patterns of the samples treated at 2073 K and 25 MPa pressure: (a) GC; (b) GCB1; (c) GCB2.

Table 3. Structural parameters obtained from the X-ray diffraction patterns presented in Fig 3.

Sample	2θ (°)	d_{002} (nm)	FWHM (°)	L_c (nm)	n
GC	26.125	0.3408	3.8	2.1	7
GCB1	26.377	0.3376	0.4	20.4	61
GCB2	26.183	0.3401	1.0	8.2	25

The absence of the B_4C reflections in the X-ray diffraction pattern of the *GCB2* sample indicates that the formation of the B_4C phase is clearly influenced by differences in the procedures conducted during the boron-containing sample preparation. Namely, when dissolving B_2O_3 in C_2H_5OH a highly reactive boron alkoxide $B(OEt)_3$ is produced [11]. It is possible that boron alkoxide chemically interacts with the resin thus incorporating boron uniformly throughout the non-polymerized and polymerized sample. This could also be a possible explanation for the appearance of B_4C only in the *GCB1* sample. Boron, chemically bonded to the polymer, can easily form the B-C bond during the carbonization processes, HTT and HTT+P treatments, while HTT and HTT+P treatments are clearly not sufficient to produce B_4C in the *GCB2* sample, where boron is present in the form of metal and/or B_2O_3.

4. Conclusions

It was shown that a substantial degree of structural ordering (*i.e.* graphitization) of glassy carbon could be obtained by adding boron into the glassy carbon precursor (resin). This approach avoids two major disadvantages of the commonly used high temperature doping process: necessary attainment of high temperature (usually 3000 K and above) and non-uniform distribution of boron throughout the bulk of the sample. Structural ordering of the glassy carbon sample obtained by adding the ethanol solution of B_2O_3 into the resin is especially efficient when high pressure is applied simultaneously with high temperature. This procedure can be used for the relatively simple synthesis

of graphitic materials and carbon/carbon composites with higher oxidation stability, taking into account that graphite is more resistant to reaction with oxygen than glassy carbon.

Acknowledgments

This research was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

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